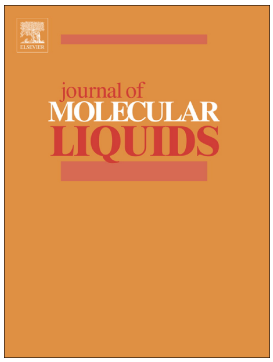

Effect of solvent nature on spectral properties of blue-emitting meso-propargylamino-BODIPY

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Effect of solvent nature on spectral properties of blue-emitting *meso*-propargylamino-BODIPY

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Abstract

The spectral and luminescent properties of *meso*-propargylamino-boron(III) dipyrromethenate (BODIPY **1**) were studied in a wide range of organic solvents of different polarities, electron- and proton-donating abilities. Effect of organic solvents on the properties of the BODIPY **1** spectral characteristics was analyzed in details. It was shown that the fluorescence of BODIPY **1** is characterized by a high sensitivity to the nature of the solvent. It was found that the complex, which emits in the blue-green region (433–486 nm), has a high quantum yield of fluorescence (~ 100%) in non-polar media (cyclohexane, benzene, toluene), while in proton- and especially electron donor media, sharp fluorescence quenching (2.2–31.2 times) of the dye is observed. For a better understanding of the spectral analysis results, a quantum-chemical analysis of the molecular structure, electronic structure, and spectral characteristics of BODIPY **1** was carried out. For the first time, it was shown that BODIPY **1** fluorescence quenching in proton and electron donor media is caused by the formation of a supramolecular dye complexes due to specific interactions of solvent molecules with atoms of the *meso*-propargylamine group. Due to practically useful spectral properties, including the sensitivity of the fluorescence to the nature of the media, BODIPY **1** is recommended as a new effective fluorescent sensor of specific electron and proton donor molecules.

Keywords

BODIPY
Meso-propargylamino-boron(III) dipyrromethenate
Spectral properties
Solvent-dependent
Fluorescence quenching
Quantum chemical analysis
One parameter and multi parameter analysis

Introduction

The active interest of scientists to fluorescent molecules is primarily due to prospects of their application in the technical and medical fields [1]. An analysis of the scientific literature cur-

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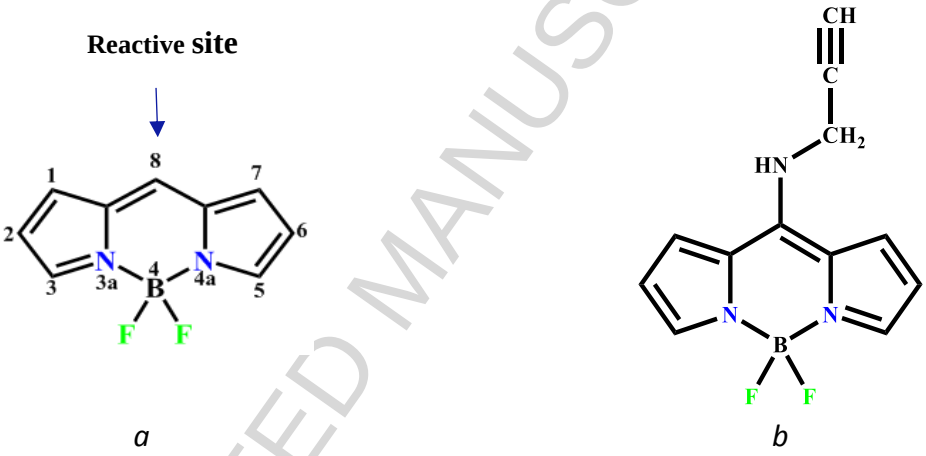
rently available shows a rapid increase in publications devoted to the group of open-chain oligopyrroles based on 4,4-difluoro-4-boron-3a, 4a-diaza-s-indacene (BODIPY) [2, 3]. Due to the excellent photophysical properties and great amenability to structural modification, these fluorophores are popular and find practical application as fluorescent markers [4, 5], fluorescent sensors [6], active media of tunable lasers [7]. The advantage of BF_2-dipyrromethenates in comparison with the known commercial dyes, for example, derivatives of the coumarin series [8], is their high photo- and chemostability [7, 9]. The main unique feature of the BODIPY structure is the completely flat and rigid chromophore core. Such a molecular structure provides a high probability of radiation deactivation and low non-radiative relaxation of the system. In addition, the dye core functionalization can be carried out in various ways [10, 11]. One of the alternative ways of influence on the chromophore and luminescent properties of this class of fluorophores is the structural modification of the substituents in the *meso*-position of the dipyrromethene core (Fig. 1 *a*). The introduction of different nature substituents into the *meso*-position makes it possible to obtain fluorophores with the spectral desired properties in a wide range of the visible spectrum [10, 11].



a *b*

Fig. 1. Representation of molecular structures: *a*) BODIPY and its IUPAC numbering system, the 8-position is often also designated *meso*; and *b*) 8-propargylamino 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY **1**).

Most of the known BODIPYs absorb and emit light in the yellow-green and red-orange regions of the visible spectrum [12, 13], although the need to create new efficient and photostable fluorophores working in the blue-green spectral region is very high. Analysis of the literature data [14] showed that a significant hypsochromic shift of the absorption and fluorescence bands maxima can be achieved by introducing nitrogen or oxygen containing substituents into the 8-position of the BODIPY. The recorded spectral bands show that the hypsochromic shift depends on the electronegativity of the attached heteroatom [3, 14]. For example, the binding of methylamine and methoxy groups led to a large hypsochromic shift of the spectral bands (i.e. 85 and 50 nm in absorption) compared to the unsubstituted dyes. Using quantum chemical calculations, the authors of [15] showed that the observed blue shift of the electronic spectra of *meso*-amino-BODIPYs is caused by a significant redistribution of electron density on atoms of the chromophore π-system of the fluorophore in the excited state compared to the ground state (Fig. 2).

It is known that the BODIPY dyes substituted to 8-position by strongly electron-donating groups such as amines are highly sensitive to the proton- and electron donation properties of solvents, leading to low fluorescence quantum yields as a consequence of intramolecular electron transfer [16]. Such a specific functionalization of the BODIPY core opens up alternative ways for the development of the new highly sensitive to the properties of the medium blue-emitting sensors.

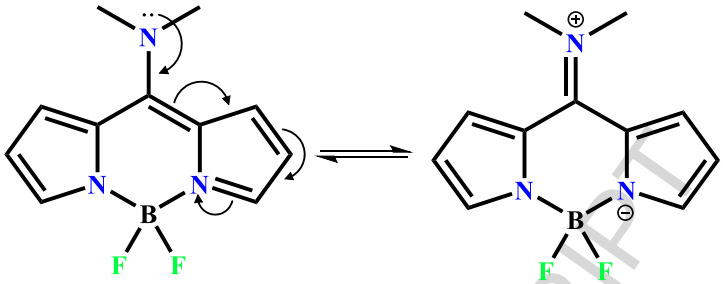


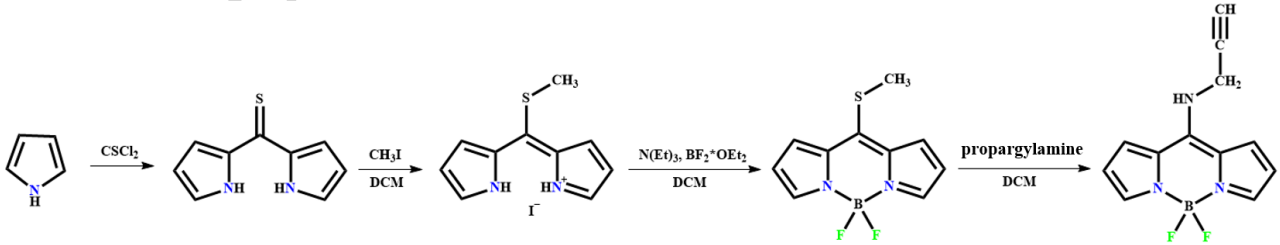
Fig. 2. Main resonant structures of the *meso*-amino-BODIPY.

Thus, we proceeded to carry out research of the *meso*-propargylamino-boron(III) dipyrromethenate (BODIPY **1**) (Fig. 1 *b*) and study in detail the dependence of its spectral properties, linking on their sensitivity to the nature of the medium, in order to enhance their practical application. We paid special attention to the study of the influence of the properties of the medium on the spectral characteristics of BODIPY **1** in a series of organic solvents of different aromaticity, proton- and electron donating ability. In addition, we carried out a detailed quantum chemical analysis of the molecular structure, electronic structure, and spectral parameters and, for the first time, showed the reasons of the dye fluorescence quenching in proton and electron donor media.

Experimental

Materials. Cyclohexane, DMF, DMSO, DEA (Panreac, Barcelona) and propanol-1 (UV-IR-HPLC-HPLC preparative PAI) were used without further purification. Other solvents (benzene, toluene, chloroform, ethanol, butanol-1) were purified according to the procedures described in [17, 18].

Synthesis. 8-Propargylamino 4, 4-difluoro-4-bora-3a, 4a-diaza-s-indacene was prepared using the techniques described in [19]. Synthesis was performed according to Scheme 1.



Scheme 1. Synthesis of 8-propargylamino 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene.

Bis-(pyrrol-2-yl)-methanethione. A solution of pyrrole (1.0 g, 14.0 mmol) in dry ether (20 ml) was added dropwise to a vigorously stirred solution of thiophosgene (0.8 g, 7.0 mmol) in dry toluene (20 ml) at 0°C. After 10 min, aqueous methanol (10%) (25 ml) was added and the mixture stirred for further 30 min at rt. The residue was dried under vacuum, then dissolved in chloroform

and chromatographed on neutral aluminum oxide. The collected fraction, after removing the solvents under reduced pressure, gives a thioketone as a crystalline orange solid. The collected fraction, after removing the solvents under reduced pressure, yieldes a thioketone as a crystalline orange solid (0,95 g, 5.4 mmol, 63%). ^{1}H NMR ($CDCl_3$): δ 6,43 (2H, CH, q, J=6.5 Hz); 7.07 (2H, CH, t, J=6.5 Hz); 7.24 (2H, CH, s); 9.81 (2H, NH, br s). Mass spectrum (EI): m/z 176 (M+); Anal. Calcd for $C_9H_8N_2S$: C 61.34, H 4.58, N 15.90. Found: C 61,42; H, 4,78; N, 15,77.

2-[Methyl sulfanyl-(1H-pyrrol-2-yl)]-2H-pyrrolium iodide. To a solution of bis-(1H-pyrrol-2-yl)-methanethione (0.60 g, 3.4 mmol) in anhydrous dichloromethane (20 ml) was added methyl iodide (0.96 ml, 15 mmol). The reaction mixture was stirred for 24 h for completion (TLC monitoring). Solvent was removed under reduced pressure to obtain brown colored gummy solid. The compound was used without further purification for the next reaction. Mass spectrum (EI): m/z 190.3 (M+).

8-(Thiomethyl)4,4-difluoro-4-bora-3a,4a-diaza-s-indacene. To a solution of 2-[methyl sulfanyl-(1H-pyrrol-2-yl)]-2H-pyrrolium iodide (0.90 g, 4.7 mmol) in anhydrous dichloromethane (25 ml) under argon atmosphere at rt was added triethylamine (3.3 ml, 7.0 mmol). After stirring for 5 min $BF_3{\cdot}OEt_2$ (3.14 ml, 25.0 mmol) was added. The mixture was stirred for 60 min at room temperature. After the evaporation of solvents under vacuum, the crude product was chromatographed on silica gel (L60/100, using 5% MeOH in dichloromethane), yielded compound as a dark red solid (0.67 g; 60%). ^{1}H NMR ($CDCl_3$): δ 2.88 (s, 3H), 6.50-6.53 (m, 2H), 7.39-7.40 (m, 2H), 7.76-7.78 (m, 2H). Mass spectrum (EI): m/z 238 (M+); Anal. Calcd for $C_{10}H_9BF_2N_2S$: C 50.45; H 3.81; N 11.77. Found: C 50.38; H 3.78; N 11.67.

8-Propargylamino 4, 4-difluoro-4-bora-3a,4a-diaza-s-indacene. To a solution of 0.5 g (2.1 mmol) of 8-(thiomethyl)4,4-difluoro-4-bora-3a,4a-diaza-s-indacene in 10 ml of dried methylene chloride was added 0.22 ml (3.15 mmol) of propargylamine. The mixture was stirred for 2 hours. The precipitate was filtered off, washed with methylene chloride and dried. The remaining solution was chromatographed on silica gel (5% methanol in chloroform), the solvent was distilled off, and the precipitate was filtered. The total yield of the product in the form of light yellow crystals was 0.38 g (1.63 mmol, 78%). λ_{max}= 415, 317 nm (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ: 2.57 (1H, CH, t, J=2.5Hz,); 4.49 (2H, CH_2, dd J=2.5 Hz, ^{1}J=5.6 Hz,); 6.52 bs, 7.13 bs, 7.67 bs (2 x 3H, *β*-H,). Mass spectrum (EI): m/z 245 (M+); Anal. Calcd for $C_{12}H_{10}BF_2N_3$: C 58.82, H 4.11, N 17.15. Found: C 58.38; H 4.09; N 17.07.

^{1}H NMR ($CDCl_3$) spectra were recorded on the spectrometer Bruker 500 (Germany).

Electronic absorption spectra of solutions of BODIPY **1** were recorded on CM 2203 spectrofluorimeter (SOLAR) in the range of molar concentrations from $1{\cdot}10^{-5}$ to $2{\cdot}10^{-6}$ mol/l and thickness of absorbing layer is 10 mm at t = 25 ± 0.1 °C.

Fluorescence spectra were obtained on CM 2203 spectrofluorimeter (SOLAR) at an optical density not higher than 0.1 at the excitation wavelength (370–400 nm).

Stokes shift was calculated as the difference between the values of maxima of the intense bands in the fluorescence and absorption spectra:

$\Delta\lambda$ (nm) = $\lambda^{fl}_{max} - \lambda^{abs}_{max}$ and $\Delta\nu_{st}$ (cm^{-1}) = $\nu^{abs}_{max} - \nu^{fl}_{max}$.

Full width at half maximum (FWHN, cm^{-1}**)** in the electronic absorption and fluorescence spectra was determined as the difference between the maximum and minimum values of the wavelengths, taken at half of intensity of $S_o \rightarrow S_1$ band.

The **fluorescence quantum yields** (φ) of BODIPY **1** were obtained with the following equation: $\varphi_{sample} = \varphi_{standard} \cdot (S_{sample}/S_{standard}) \cdot (A_{standard}/A_{sample}) \cdot (n_{sample}/n_{standard})^2$,
where *S* denotes the area under the fluorescence band of sample (BODIPY **1**) and standard (Coumarin 102), *A* denotes the absorbance of sample and standard at the excitation wavelength, and *n* denotes the refractive index of the solvent. The standard for measuring the fluorescence quantum yield is Coumarin 102 in ethanol (φ = 76.4%) [20, 21].

The **fluorescence lifetime** (τ) was estimated based on the spectral-luminescent characteristics. In accordance with $\varphi = k_{rad}/(k_{rad} + k_{nr})$ and $\tau = 1/(k_{rad} + k_{nr})$, fluorescence lifetime was determined by: $\tau = \varphi/k_{rad}$, where k_{nr} is the rate of non-radiative processes, k_{rad} is rate of radiative processes (radiation constant), the fluorescence lifetime error is ~10–15%. The **rate constant of radiative processes** was estimated from the characteristics of the electronic absorption spectra in accordance with the [20]: $k_{rad} = 2.9 \cdot 10^{-9} \cdot [(9n_D^2)/(n_D^2+2)^2] \cdot \nu_{max}^2 \cdot \varepsilon_{max} \cdot \Delta\nu_{1/2}$, where n_D is the refractive index of the solvent, ν is wave number of absorption band maximum (cm^{-1}); $\Delta\nu_{1/2}$ is half-width of the absorption band (cm^{-1}); ε is extinction coefficient of intense absorption band. The **rate constant of nonradiative deactivation** (k_{nr}) was calculated from experimentally measured fluorescence quantum yield and fluorescence lifetime according to the following equations: $k_{nr} = (1 - \varphi)/\tau$.

The **function of universal interactions** (Δf), used as a solvent polarity parameter, was calculated according to the equation of Lippert [21]:

$\Delta f = f(\varepsilon) - f(n_D^2) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{n_D^2 - 1}{2n_D^2 + 1}$, where ε is dielectric constant, n_D is the refractive index of the solvent. The $f(\varepsilon)$ is total polarization and $f(n_D^2)$ is induction polarization.

Table 1. Polarity/polarizability, acidity, basicity parameters and Gutman's electron-donor and acceptor numbers of organic solvents

Solvent	ε	μ	Δf	E_T^N	*DN*	*AN*	*SPP*	*SB*	*SA*	*a*	*b*	π*
cyclohexane	2.024	0	0.002	0.01	–	0	0.557	0.07	0	0	0	0
benzene	2.3	0	0.003	0.11	0.1	8.2	0.667	0.12	0	0	0.10	0.59
toluene	2.38	0.31	0.014	0.10	0.001	–	0.655	0.13	0	0	0.11	0.54
chloroform	4.9	1.15	0.150	0.26	4.8	23.1	0.786	0.07	0.05	0.2	0.1	0.58
butanol-1	17.1	1.68	0.263	0.6	19.5	36.8	0.84	0.81	0.34	0.84	0.84	0.47
propanol-1	20.3	1.68	0.270	0.62	20	37.3	0.847	0.78	0.37	0.84	0.9	0.52
ethanol	24.3	1.66	0.290	0.65	19.6	37.9	0.853	0.66	0.4	0.86	0.75	0.54
DMF	36.7	3.86	0.280	0.40	26.6	16	0.954	0.61	0.03	0	0.69	0.88
DMSO	45.0	3.96	0.263	0.44	29.8	19.3	1.0	0.65	0.07	0	0.76	1
DEA	12.5	0.92	0.252	0.15	50	9.4	-	-	-	0.3	0.7	0.24

***Notes*:** ε is dielectric constant, μ – dipole moment, (D), Δf – empirical Lippert parameter [20], E_T^N – normalized Dimroth-Reichardt parameter [22]; *a*, *b*, π* – Kamlet-Taft solvent parametrs; *SPP* – polarity/polarizability, *SB* – basicity and *SA* – acidity Catalán solvent parameters [22], *DN* and *AN* – Gutman's electron-donor and acceptor numbers [24].

Quantum chemical calculations. All the quantum mechanical calculations were performed by means of the PC GAMESS US v. 12 program package [25]. Ground (GS) and excited (ES) state

geometries were fully optimized by wB97X-D/6-311++G (d,p) [26–28]. Absorption transitions were simulated using TD-CAMB3LYP/6-311++G(d,p) [29]. The polarizable continuum model (PCM) applying dielectric constants of cyclohexane, chloroform, benzene, toluene, ethanol, propanol, butanol, DMF, DMSO, and DEA allowed to evaluate solvation effects [30]. The ChemCraft 1.8 was used for analyses of results and molecular graphics [31].

Results and discussion

The **spectral characteristics** of the BODIPY **1** in a series of organic solvents are presented in Table 2, the electronic absorption and emission spectra are shown in Fig.3.

Table 2. Spectral characteristics of BODIPY **1** in organic solvents

Solvent	λ^{abs}_{max} (ε), $S_0 \rightarrow S_1$ $S_0 \rightarrow S_2$	FWHN, cm^{-1} Abs	λ^{fl}_{max}, $S_1 \rightarrow S_0$	$\Delta\lambda_{st}$	φ (λ_{ex}) $S_1 \rightarrow S_0$	$k_{rad}\cdot10^{-7}$, s^{-1}	$k_{nr}\cdot10^{-7}$, s^{-1}	τ, ns
cyclohexane	426(41316) 318(18075)	1695	486	60	0.999 (400)	15.72	0.02	6.36
benzene	422(43771) 321(18913)	1843	485	63	0.924 (400)	14.72	1.21	6.28
toluene	421(42912) 322(20113)	1781	485	64	0.92 (395)	14.02	1.22	6.56
chloroform	418(42228) 320(22180)	1997	485	67	0.829 (395)	15.66	3.23	5.29
butanol-1	406(32496) 319(18137)	2040	463	57	0.790	13.12	3.49	6.02
propanol-1	408(34962) 318(19223)	2097	467	59	0.741 (395)	14.36	5.02	5.16
ethanol	406(33530) 318(16444)	2186	468	62	0.600 (395)	14.48	9.66	4.14
DMF	404(34821) 319(15790)	2255	458	54	0.442 (395)	14.82	18.73	2.98
DMSO	404(35641) 320(17396)	2323	463	59	0.278 (395)	16.11	41.73	1.73
DEA	405(33921) 319(17298)	2357	433	28	0.032 (370)	15.89	48.16	0.20

Notes: λ^{abs}_{max} λ_{ex} – absorption, excitation and fluorescence maxima, respectively, nm; ε – molar absorption coefficient (L mol cm^{-1}); FWHN is full width at half maximum in the electronic absorption spectrum (cm^{-1}); $\Delta\lambda_{st}$ – Stokes shift, nm; φ – fluorescence quantum yield; k_{rad}, k_{nr} – rate constants of radiative process and nonradiative deactivation, respectively, s^{-1}; τ – fluorescence lifetime, ns.

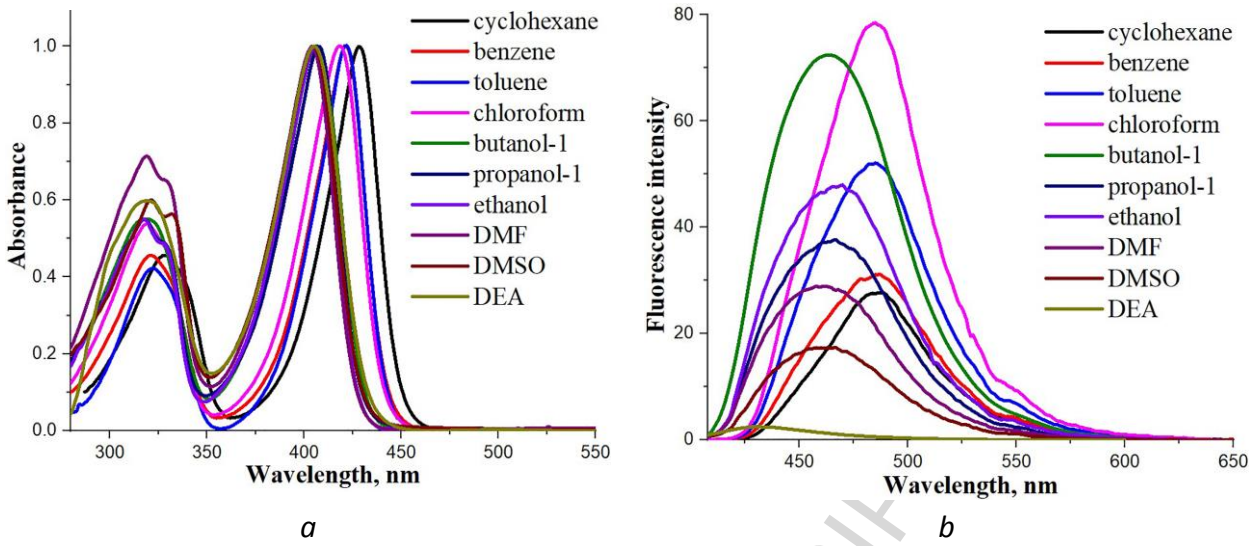
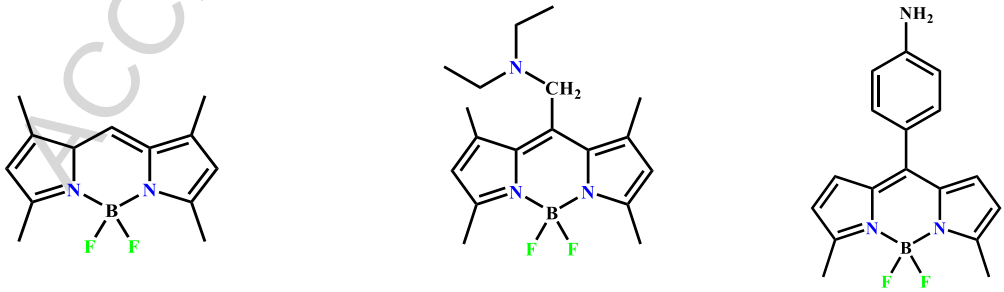


Fig. 3. Normalized electronic absorption spectra (*a*) and electronic emission spectra (*b*) of BODIPY **1** solution in organic solvents.

The absorption bonds of BODIPY **1** are placed in the blue-green region in all solvents studied (Table 2, Fig. 3 *a*). The high-intensity $S_0 \rightarrow S_1$ band is in the range of 404–426 nm. A less intense $S_0 \rightarrow S_2$ band with shoulders on the right and left slopes is recorded in the shorter wavelength region (315–322 nm) (Fig. 3). The molar extinction coefficient of the $S_0 \rightarrow S_1$ band (33530–43771 l/mol · cm) (Table 2) is almost 1.5–2 times lower than for the alkyl-substituted BODIPYs [32].

The introduction of the propargylamino group into the *meso*-position shifts the absorption and fluorescence bands maxima of BODIPY **1** by almost 100 nm to the shortwave region (Table. 2, 3) compared with the *meso*-unsubstituted analog 3,3',4,4'- tetramethylalkylated BODIPY **2** [32] and boron(III) dipyrromethenates with *meso*-substituents: $–CH_2–N(C_2H_5)_2$ in BODIPY **3** [33] and $–Ph–NH_2$ in BODIPY **4** [34], in which the electron pair of the unhybridized *p*-orbital of an amino group nitrogen atom is isolated from the conjugated chromophore system due to $–CH_2–$ and –Ph– fragments:



BODIPY **2**[32] BODIPY **3**[33] BODIPY **4**[34]

	C_2H_5OH	C_2H_5OH	CH_2Cl_2
λ^{abs}_{max} (λ^{fl}_{max}), nm	503 (512)	497 (513)	507(523)
φ	0.88	0.015	0.198.

The fluorescence spectra (after excitation at 370-395 nm*)* of the *meso*-propargylamino-BODIPY **1** are the mirror reflections of the high-intensity $S_0 \rightarrow S_1$ bands with a significant Stokes shift

$\Delta\lambda_{st}$ = 28–67 nm, (Fig. 3 *b*, Table 2), while for alkyl-substituted analogs, the value $\Delta\lambda_{st}$ is usually small and fluctuates in the range of 5–10 nm [32]. The observed large Stokes shift and the broadened shape of the emission band (Table 2, Fig. 3 *b*) indicate a significant difference in the geometry of the excited state relative to the ground state of BODIPY **1**.

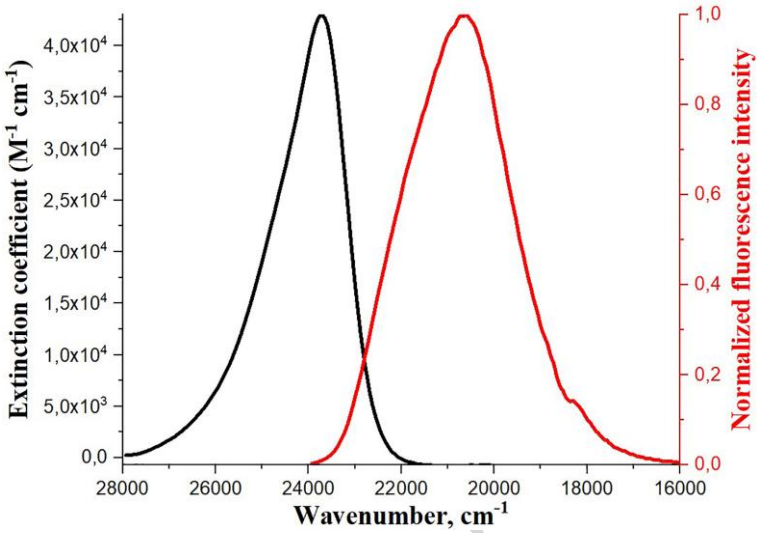
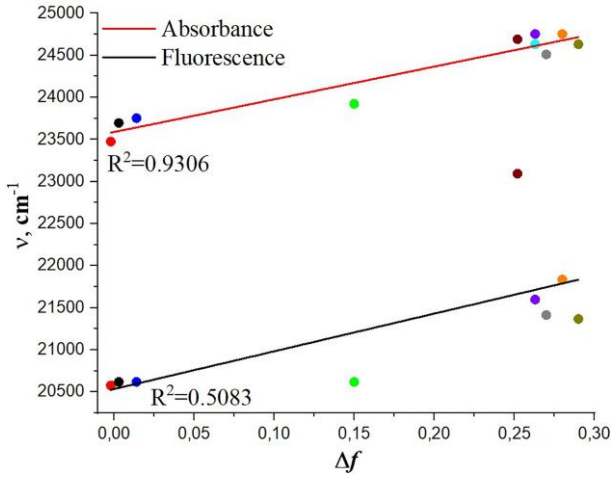


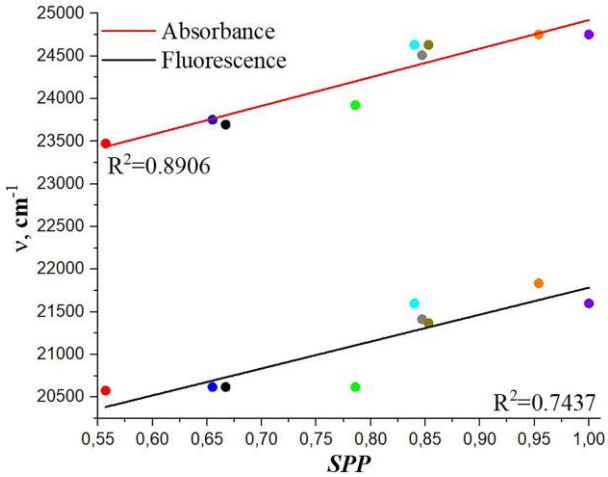
Fig. 4. Absorption and normalized fluorescence spectra of BODIPY **1** in toluene (λ_{ex}= 395 nm).

Analysis of the solvatochromic and solvatofluoric effects showed a high sensitivity of the spectral characteristics of BODIPY **1** to the properties of the medium, which is not typical for most alkyl-substituted BODIPY [35, 36].

The effect of solvent nature on the position of the maximum of the intense absorption and fluorescence bands (ν, cm^{-1}), Stokes shift ($\Delta\nu$, cm^{-1}), fluorescence quantum yield (φ) and lifetime (τ) of BODIPY **1** were analyzed using polarity/polarizability, acidity (*SA*), basicity (*SB*) parameters, Gutman's acceptor and electron-donor numbers of the solvent (Table 2, 3). Figure 5 shows the dependences of the spectral characteristics on the Lippert, Dimrot-Reichardt, Catalan parameters and Gutman's acceptor and electron-donor numbers.



a



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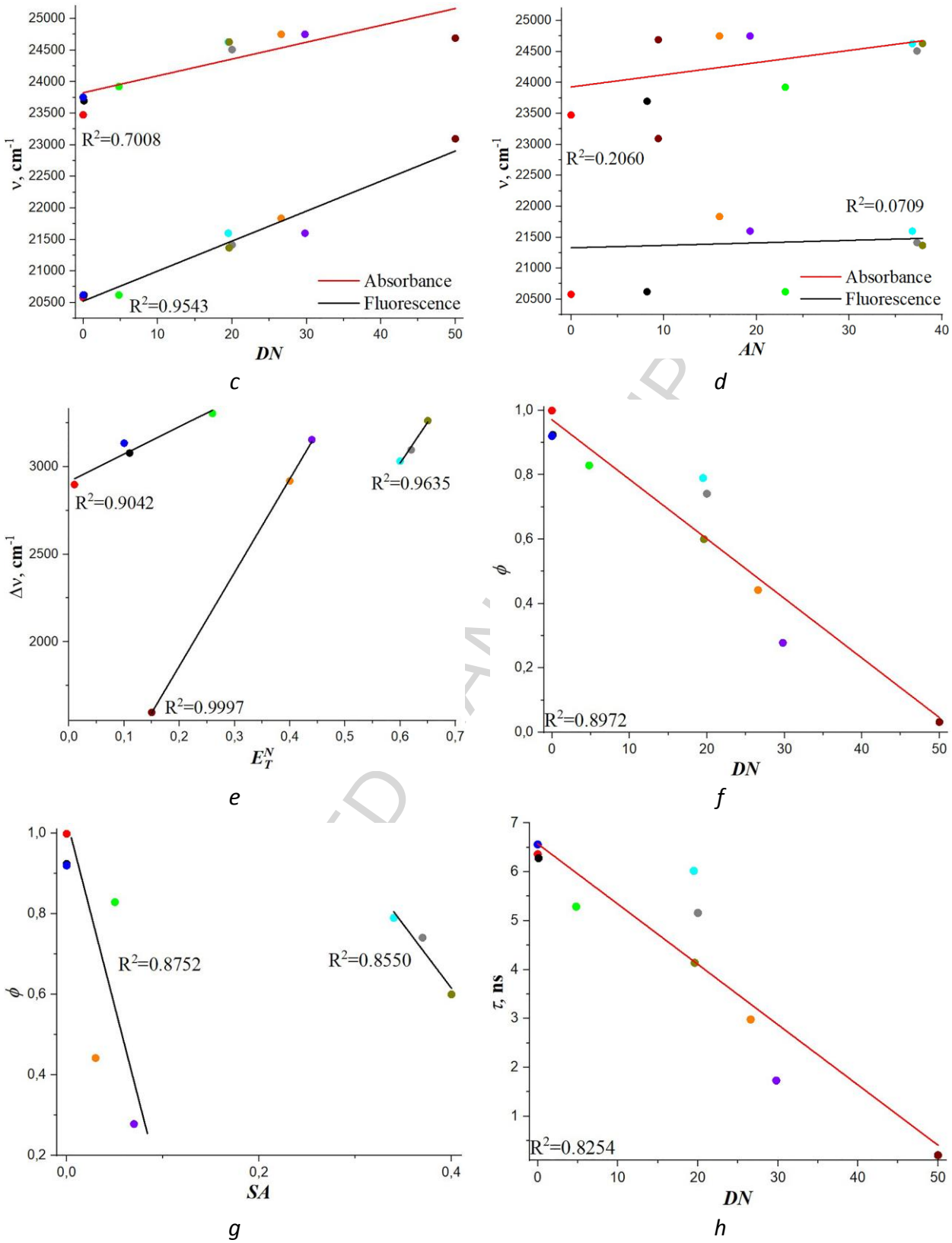

Fig. 5. Dependences of spectral characteristics of BODIPY **1** on parameters of solvent polarity Lippert (Δ*f*), Dimroth-Reichardt (E_T^N), Catalan (*SPP*, *BS*, *AS*) and Gutman's acceptor and electron-donor numbers (*DN* and *AN*): ν = Δ*f* (a); ν = *SPP* (b); ν = *DN* (c); ν = *AN* (d); Δν = E_T^N (e); *φ* = *DN* (f); *φ* = *SA* (g); *τ* = *DN* (h); (where ● – cyclohexane, ● – benzene, ● – toluene, ● – chloroform, ● – butanol-1, ● – propanol-1, ● – ethanol, ● – DMF, ● – DMSO, ● – DEA).

In the general case, with the increase of Δ*f*, *SPP* and *DN*, the absorption and fluorescence bands maxima are shifted towards short waves and the relative quantum yields and fluorescence lifetime decrease (Fig. 4 *a*-*c*, *f* and *h*). Sufficiently high values of the approximation coefficients were obtained for the dependences of the spectral characteristics on the Lippert and Catalan parameters (R^2 = 0.9306–0.7437), which indicates a significant contribution of specific interactions to the solvatofluoric and solvatochromic effects of BODIPY **1**. The best correlation of the dependences of the spectral characteristics is observed with the Gutman's electron-donor number (R^2 up to 0.9543, Fig. 5 *c*). The R^2 values for the spectral characteristics dependences on *AN* are significantly lower and do not exceed ~ 0.2060 (Fig. 5 *d*). The good correlation is observed while using the SA parameter, which takes into account the acid-base interactions of dissolved compound with the solvent. The group of alcohols (ethanol, propanol-1, butanol-1) is allocated in a separate area on this dependence (Fig. 5 *g*). It should be noted that on the dependences of Δν values on the considered solvent parameters, including E_T^N (Fig. 5 *e*), three areas for non-polar and weakly polar (cyclohexane, benzene, toluene, chloroform), electron-donor (DMSO, DMF, DEA) and proton-donor (ethanol, propanol-1, butanol-1) solvents are released. The obtained results suggest significant differences in the geometry of the excited and ground state of BODIPY **1** caused by the specific solvation of the luminophore due to acid-base interactions of electron-donor heteroatoms with the acetylene proton (*Solv*)O**:**⋯H-C≡C– and proton of –OH group of alcohols with an electron-donating nitrogen pair of the amino group (*Solv*)OH⋯**:**N≤. This assumption was confirmed by the results of quantum chemical calculations, which are presented in the next section. Analyzing the obtained data, it can be noted that the strongest influence on the spectral characteristics of BODIPY 1 is provided by solvents with pronounced electron donor properties. Narrowing of the intense band of the electronic absorption spectrum is observed in the transition from polar to nonpolar media (Table 2). The FWHM values for the complex in DEA are 2357 cm^{-1} and decrease by more than 662 cm^{-1} in cyclohexane (1695 cm^{-1}). The transfer from inert cyclohexane to electron donor DMF, DMSO and DEA is accompanied by a short-wave shift of the maxima of the absorption (fluorescence) bands on ~ 21–22 (23–53) nm and sharp quenching of the dye fluorescence (*φ* decreases in ~2.2–31.2 times) (Table 2). A smaller decrease in the fluorescence quantum yield is observed in alcohols (in ~1.3–1.7 times). This indicates a higher sensitivity of BODIPY **1** fluorescence to the presence, especially, of electron-donating compounds.

The fluorescence lifetime of the BODIPY **1** in the excited state is significantly reduced (from 6.36 to 1.73 ns) when replacing non-polar media with proton- and electron-donor solvents (Table 2). At the same time, the value of the radiative processes constant (k_{rad}) has little dependence on the properties of the medium (Table 2). Changing the nature of the medium has significant effect on the values of nonradiative deactivation constants of BODIPY **1**. For example, the k_{nr} values increase in ~2400 times when replacing an inert cyclohexane with electron donor diethylamine.

A more correct description of effect of solvent nature on spectral properties should be carried out using a multiparameter solvent scales, taking into account solvent polarity, polarizability, proton and electron donating properties, with the linear regression method:

$X = X_0 + aA + bB + cC + \ldots$,

where X – physical or chemical characteristic depending on the solvent (ν_{abs}, ν_{fl} and $\Delta\nu$); X_0 – value of the physical or chemical property in the gas phase, or ‘‘standard’’ (inert) solvent; A, B and C –

independent but complementary solvent parameters (polarity, polarizability proton or electron donating and other properties), describing various mechanisms of interaction of the solvent with the solute; *a*, *b* and *c* – coefficients characterizing the contribution of the parameters A, B and C of the solvent in the property studied.

Application of the linear regression analysis method allows determining the contributions of the individual parameters of the solvents in the photophysical characteristics of the solute, taking into account their impact quantitatively. The most commonly used parameter sets are the parameters proposed by Kamlet and Taft – the scale of polarity/polarizability of the solvent (π^*), scale of proton-donor properties of the solvent (*a*) and electron-donor properties scale (*b*) [37], as well as a set of Catalan parameters – the scale of polarity/polarizability of the solvent (SPP), acidity solvent scale (SA) and basic solvents scale (SB) [23]. The values of each parameter vary from 0 to 1. X_0 parameter is the free term of the linear equation; it was taken as the property of the investigated molecules in the gas phase.

Higher coefficients of determination of linear correlation were obtained for used solvent parameter sets in comparison with the one-parameter correlations (Fig. 5), that means the applicability of the taken model and chosen set of parameters (Table 3).

Table 3. Calculated parameter values in gas phase (X_o), correlation coefficients of the linear regression (*a*, *b*, *c*), and (R^2) are values of coefficients of determination

Kamlet and Taft parameters					
X	X_0,	*a*(**π***)	*b*(***a***)	*c*(***b***)	R^2
φ	0.820±0.165	0.322±0.308	0.707±0.277	-1.115±0.31	0.5672
$\boldsymbol{\lambda}^{abs}_{max}$, cm^{-1}	23561.65±124.12	152.26±232.14	-252.56±208.33	1444.37±233.61	0.9047
$\boldsymbol{\lambda}^{fl}_{max}$, cm^{-1}	21129.95±347.08	1546.70±649.15	1492.63±582.56	3009.35±653.26	0.6931
$\boldsymbol{\Delta\lambda_{st}}$, cm^{-1}	2434.70±260.99	1698.97±488.14	1240.09±438.06	-1564.99±491.22	0.5536
Catalan parameters					
X	X_0,	*a*(**SPP**)	*b*(**SA**)	*c*(**SB**)	R^2
φ	1.914±0.282	-1.497±0.440	0.430±0.359	-0.137±0.284	0.8454
λ^{abs}_{max}, cm^{-1}	22267.34±231.48	2070.36±361.40	99.24±94.82	710.33±233.41	0.9772
λ^{fl}_{max}, cm^{-1}	20008.41±356.49	685.99±556.57	1107.67±454.02	1705.68±359.46	0.9469
$\Delta\lambda_{st}$, cm^{-1}	2258.93±224.43	1384.38±350.39	1206.95±285.83	-995.37±226.30	0.6998

Better linear regression accuracy could be achieved in the case of the Catalan parameters. Nature of the spectral characteristics dependence on the parameters of solvents is complex. Negative values of the *a* and SA parameters for the absorption and fluorescence maxima indicate a hypsochromic shift in the spectra with an increase in the electrophilic properties of the solvent. Strengthening the proton- and electron donor properties of the solvent leads to a hypsochromic shift of the absorption maxima and reducing the Stokes shift in comparison with inert solvents. Linear regression analysis allows us to conclude that parameters *b* and SB make a greater contribution in the spectral characteristics for obtaining the best correlation. Solvent parameters *a* and SA

also contribute to the spectral characteristics of the luminophore under study, but to a much smaller extent.

The observed high fluorescence sensitivity of BODIPY **1** to electron and proton donor compounds favorably distinguishes the synthesized fluorophore from most alkyl analogs [32, 35], what is of considerable interest in the development of new fluorescent sensors based on *meso*-amino-BODIPYs to the presence of specifically solvating electron- and proton-donor molecules.

Computational modeling. To better understanding of spectroscopic measurements results, computational modeling was carried out. The computed absorption spectra of BODIPY **1** show four bands of different intensity caused by the S_0-S_n electronic transitions (Table S1, Fig. 6).

The most intense S_0–S_1 absorption band has a maximum in the range of 351–364 nm (depending on the solvent). This band caused by the HOMO–LUMO transition. The HOMO is the electron density localization at the BODIPY core. The LUMO is localized at the BODIPY core and the nitrogen atom of the propargylamine group. In the range of 268–285 nm there are the bands belonging to S_0–S_2, S_0–S_3 electronic transition (HOMO-1–LUMO, HOMO-2–LUMO, respectively); in the range of 253–257 nm the S_0–S_4 band (HOMO-3–LUMO) is registered.

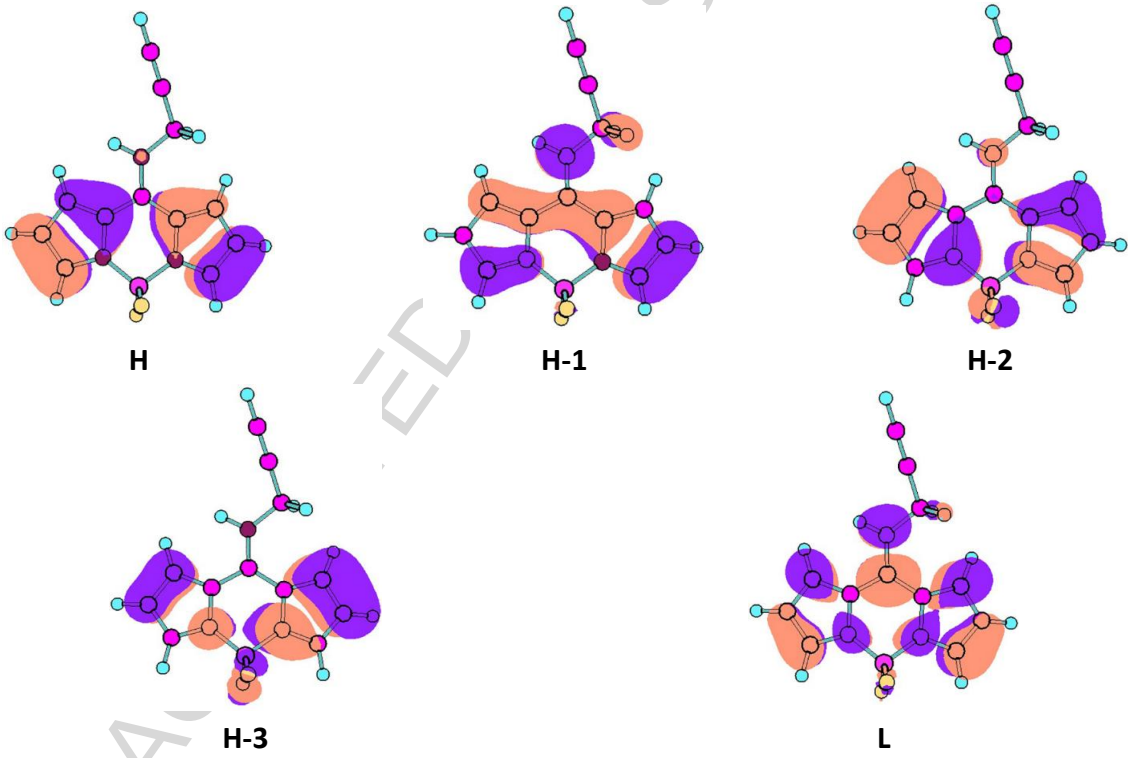

Fig. 6. FMOs of BODIPY **1**.

The intense S_0–S_1 absorption band is most sensitive to the solvent nature (Table S1). This band is shifted to the blue region at the transition from non-polar to polar solvents (Table S1). It is shown fluorescence of BODIPY **1** is quenched in proton- and electron-donor solvents. Guo et al have showed fluorescence quenching of BODIPYs with electron-donor groups in *meso*-position (in $CHCl_3$ and ethanol) is due to photoinduced electron transfer from the electron-donor group to the BODIPY core [38]. Thus in BODIPY **1**, the HOMO of propargylamine group is higher in energy than the HOMO

of BODIPY core. When photoexcited, the electron transfer from the HOMO of propargylamine group to the HOMO of BODIPY core is energetically favorable (Fig. 7).

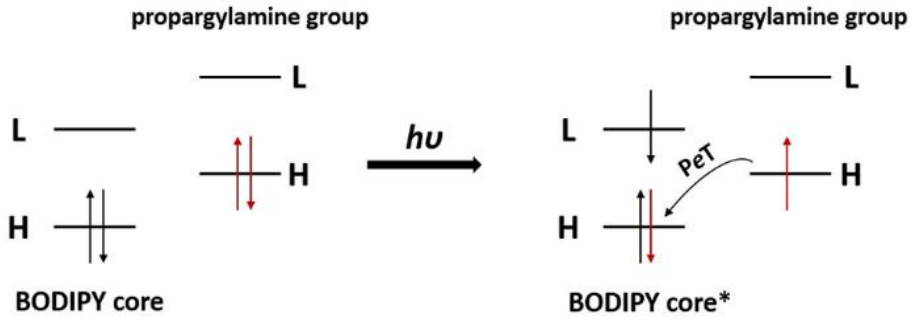

Fig. 7. Photoinduced electron transfer mechanism of BODIPY **1**.

However, this paper [38] does not consider mechanism of the influence of the solvent molecules on the BODIPYs fluorescence quenching. It can be assumed the BODIPY **1** fluorescence quenching is associated with solvation increase by proton- and electron-donor solvents of BODIPY **1** in the excited state. The reason for this phenomenon is the excess negative charge on the nitrogen atom of the amino group and the positive charge on the hydrogen atom of methine group of BODIPY **1** in the excited state. This creates the conditions for the formation of BODIPY **1** supramolecular complexes with proton- and electron-donor molecules ([BODIPY **1**·X], where X – chloroform, ethanol, propanol, butanol, DMF, DMSO, DEA) (Fig. 8). Molecular modeling of [BODIPY **1**·X] showed the proton-donor molecules (chloroform, ethanol, propanol) are coordinated on the nitrogen atom of BODIPY **1** propargylamine group to form H···N hydrogen bond while the electron-donor molecules are coordinated on the acetylene group hydrogen atom of BODIPY **1** propargylamine group to form the H···O hydrogen bond (DMF, DMSO) and to form the H···N hydrogen bond (DEA) (Fig. 8, Table 4). It is important to note, in contrast to ethanol and propanol, in the case of butanol, it is not the proton that participates in the interaction with the luminophor, but the oxygen atom of the hydroxyl group. This is evidenced by the relatively small distance between the oxygen of the OH-group of butanol and the proton of the acetylene BODIPY **1** residue (it is comparable to that in solvate complexes with DMF and DMSO ([BODIPY **1**·X]) (Fig. 8, Table 4). Obviously, this type of interaction is realized by reducing the acidic properties of the butanol hydroxyl group in comparison with precursors with a shorter carbon chain [39]. In addition, the possibility of the formation of weak orientational interactions between the nitrogen atom of BODIPY 1 propargylamine group and the OH-group hydrogen atom of butanol remains (Fig. 8, Table 4). Supramolecular complexation increases the nonradiative transitions probability. It leads to the BODIPY **1** fluorescence quenching in proton- and electron-donor solvents.

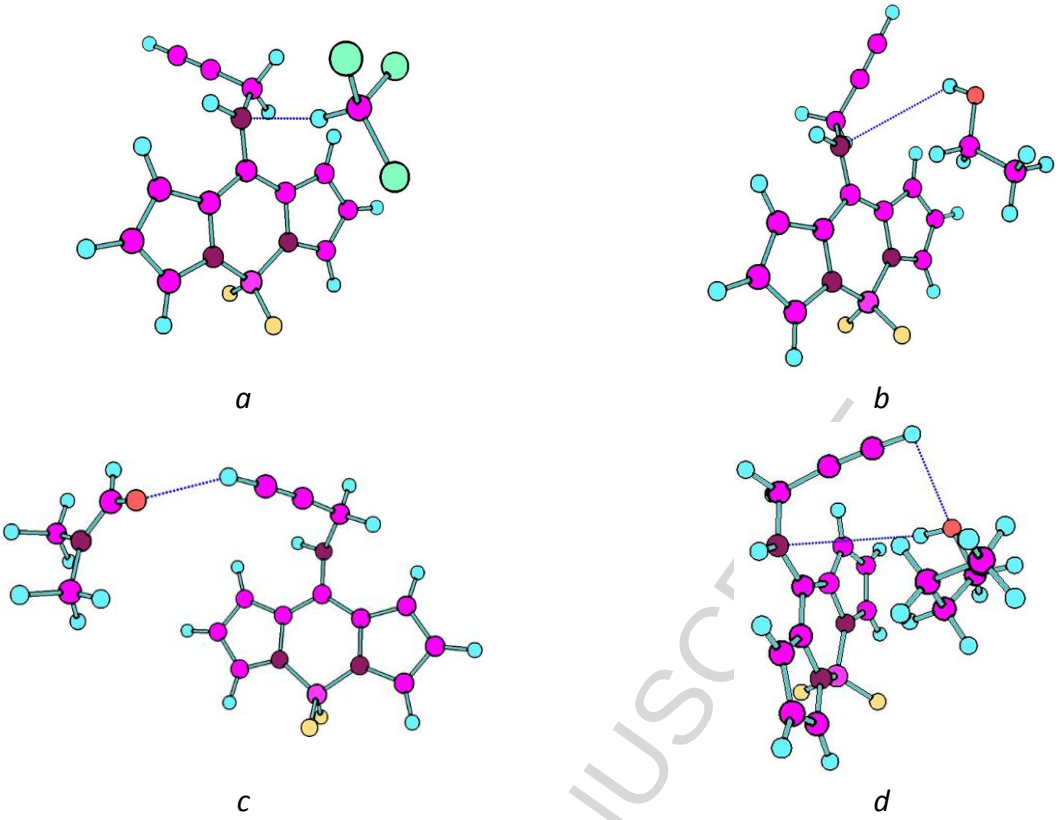

Fig. 8. Structures of supramolecular complexes formed by BODIPY **1** with chloroform (*a*), ethanol (*b*), DMF (*c*), and butanol (*d*).

The dipole moments of the ground (GS) and excited (ES) state of BODIPY **1** and supramolecular complexes formed by BODIPY **1** with proton- and electron-donor molecules ([BODIPY **1**·X], where X – chloroform, ethanol, propanol, butanol, DMF, DMSO, and DEA) are given in Table 4.

Table 4. Calculated the structural parameters of the GS and ES of BODIPY **1** and [BODIPY **1**·X] dipole moments (μ, D) and distance between the X molecule and BODIPY **1** (*l*, Å).

System	GS		ES	
	l, Å	μ	*l*, Å	μ
BODIPY **1**	-	7.64	-	7.62
(chloroform)H···N(BODIPY **1**)	2.373	6.16	2.391	5.95
(ethanol)H···N(BODIPY **1**)	3.684	7.24	3.512	7.29
(propanol)H···N(BODIPY **1**)	2.973	5.60	3.644	6.71
(butanol)H···N(BODIPY **1**) (butanol)O···H(BODIPY **1**)	4.104 2.825	6.08	4.173 2.911	5.99
(DMF)O···H(BODIPY **1**)	2.274	7.44	2.119	7.59
(DMSO)O···H(BODIPY **1**)	1.998	6.64	1.991	6.39
(DEA)N···H(BODIPY **1**)	3.686	7.05	3.783	6.97

The supramolecular complexes formation results in BODIPY **1** chromophore system depolarization. This cause to the stabilization of BODIPY **1** in the ground and excited state in proton- and electron-donor solvents. The stabilization effect of BODIPY **1** is accompanied by a blue shift of the

absorption and emission spectra maxima of BODIPY **1** in proton- and electron-donor solvents.

Conclusion

Thus, the spectral analysis showed that the synthesized *meso*-propargylamino-BODIPY **1** exhibits a high sensitivity of the spectral characteristics to the properties of the medium, this is not typical for most of the known alkyl-substituted analogues. It was found that the complex, emitting in the blue-green region (458–486 nm), has a high fluorescence quantum yield (almost ~ 100%) in non-polar media (cyclohexane, benzene, toluene), while in proton- and especially in electron donating media, sharp quenching of the fluorescence (2.2–31.2 times) of the dye is observed. One parameter and multi parameter approaches were used for describing solvent influence on spectral properties of the BODIPY **1**. Quantum-chemical analysis showed that the reason for quenching of fluorescence of the synthesized fluorophore in proton- and electron-donor media is the formation of supramolecular complexes due to acid-base interactions of molecules of electron-donor solvents and alcohols with atoms of the *meso*-propargylamine group. The obtained results allow us to propose the BODIPY **1** as a potential highly sensitive sensor of electron and proton donor compounds.

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References

[1] L.M. Wysocki, L.D. Lavis. Advances in the chemistry of small molecule fluorescent probes, Curr. Opin. in Chem. Biol. 15 (2011) 752–759. doi:10.1016/j.cbpa.2011.10.013.

[2] V. Lakshmi, R. Sharma, M. Ravikanth. Functionalized boron-dipyrromethenes and their applications, Rep. in Org. Chem. 6 (2016) 1–24. doi:org/10.2147/ROC.S60504.

[3] I. Esnal, I. Valois-Escamilla, C.F. Gómez-Durán, A. Urías-Benavides, M. L. Betancourt-Mendiola, I. López-Arbeloa, J. Bañuelos, I. García-Moreno, A. Costela, and E. Peña-Cabrera. Blue-to-Orange Color-Tunable Laser Emission from Tailored Boron-Dipyrromethene Dyes, ChemPhysChem. 14 (2013) 4134 – 4142. doi: 10.1002/cphc.201300818.

[4] N. Boens, V. Leen, W. Dehaen. Fluorescent indicators based on BODIPY, Chem. Soc. Rev., 41 (2012) 1130–1172. doi: 10.1039/C1CS15132K.

[5] A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess. BODIPY dyes in photodynamic therapy, Chem. Soc. Rev. 42 (2013) 77–88. doi:10.1039/c2cs35216h.

[6] S. Zhu, J. Zhang, J. Janjanam, G. Vegesna, F.-T. Luo, A. Tiwari, H. Liu. Highly water-soluble BODIPY-based fluorescent probes for sensitive fluorescent sensing of zinc(II). J. Mater. Chem. B. 1 (2013) 1722–1728. doi:0.1039/C3TB00249G.

[7] A. Costela, I. García-Moreno, M. Pintado-Sierra, F. Amat-Guerri, R. Sastre, M. Liras, López Arbeloa F., J. BañuelosPrieto, I. López Arbeloa. New analogues of the BODIPY dye PM597: photophysical and lasing properties in liquid solutions and in solid polymeric matrices, J. Phys. Chem. A. 113 (2009) 8118-8124. doi:10.1021/jp902734m.

[8] N.G. Bryantseva, I.V. Sokolova, A.B. Tsyrenzhapova, N.I. Selivanov, V.P. Khilya, Ya.L. Garazd Fluorescent characteristics of coumarin photosensitizers, J. of App. Spec. 75 (2008) 700-705. doi:10.1007/s10812-008-9100-z.

[9] D.A. Merkushev, S.D. Usoltsev, Yu.S. Mar, A.P. Pushkarev, D. Volyniuk, J.V. Grazulevicius, E.V. Rumyantsev. BODIPY associates in organic matrices: Spectral properties, photostability and evaluation as OLED emitters, Mat. Chem. and Phys. 187 (2017) 104–111. doi:org/10.1016/j.matchemphys.2016.11.053.

[10] V. Lakshmi, R. Sharma, M. Ravikanth. Functionalized boron-dipyrromethenes and their applications, Rep. in Org. Chem. 6 (2016) 1–24. doi:org/10.2147/ROC.S60504.

[11] G. Ulrich, R. Ziessel, A. Harriman, The Chemistry of Fluorescent Bodipy Dyes: Versatility Unsurpassed. Angew, Chem. Int. Ed. 47 (2008) 1184–1201. doi:10.1002/anie.200702070.

[12] A.Yu. Nikonova, R.T. Kuznetsova, Iu.V. Aksenova, E.N. Tel'minov, G.V. Mayer, N.A. Dudina, E.N. Nuraneeva, and E.V. Antina. Optical Properties of Zinc(II) and Boron(III) Dipyrrinates with Different Structures, Opt. and Spec. 120 (2016) 395–402. doi: 10.1134/S0030400X16030176.

[13] H. Lu, J. Mack, Y. Yang and Z. Shen. Structural modification strategies for the rational design of red/NIR region BODIPYs, Chem. Soc. Rev. 43 (2014) 4778– 4823. doi: 10.1039/c4cs00030g.

[14] Yu Gabe, Y. Urano, K. Kikuchi, H. Kojima, and T. Nagano. Highly Sensitive Fluorescence Probes for Nitric Oxide Based on Boron Dipyrromethene Chromophores Rational Design of Potentially Useful Bioimaging Fluorescence Probe, J. Am. Chem. Soc. 126 (2004) 3357-3367. doi: 10.1021/ja037944j.

[15] J. Bacuelos, V. Martyn, C.F.A. Gymez-Durán, I.J.A. Córdoba, E. Peca-Cabrera, I. García-Moreno, Á. Costela, M.E. Pérez-Ojeda, T. Arbeloa, H. López-Arbeloa. New 8-Amino-BODIPY Derivatives: Surpassing Laser Dyes at Blue-Edge Wavelengths. J. Chem. Eur. 17 (2011) 7261-7270. doi:10.1002/chem.201003689.

[16] R.I. Roacho, A. Metta-Magaña, M.M. Portillo, E. Peña-Cabrera, and K.H. Pannell. 8-Amino-BODIPYs: Structural Variation, Solvent-Dependent Emission, and VT NMR Spectroscopic Properties of 8-R_2N-BODIPY, J. Org. Chem. 78 (2013) 4245−4250. doi:org/10.1021/jo302758a.

[17] Gordon, R. Ford. Sputnik Chimica. Mir, Moscow. (1976) 529.

[18] J.A. Riddick, W.B. Bunger, T.K. Sakano. Organic solvents: physical properties and methods of purification. (1986) 1325.

[19] T.V. Gouda, A. Tutar, J.F. Biellmann. Synthesis of 8-heteroatom-substituted 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene dyes (BODIPY), Tetrahedron. 62 (2006) 5084-5091. doi: 10.1016/j.tet.2006.03.036.

[20] M. Fischer, J. Georges. Fluorescence quantum yield of rhodamine 6G in ethanol as a function of concentration using thermal lens spectrometry, Chem. Phys. Lett. 260 (1996) 115–118. doi: org/10.1016/0009-2614(96)00838-X.

[21] O.S. Wolfbeis. Standardization and Quality Assurance in Fluorescence Measurements Techniques, Springer Ser. Fluoresc. (2008) 101–145.

[22] J.R. Lakowicz. Principles of fluorescence spectroscopy. Springer Science & Business Media, (2006) 954.

[23] J. Catalan, V. Lopez, P. Perez. Use of the SPP scale for the analysis of molecular systems with dual emissions resulting from the solvent polarity, J. Fluoresc. 6 (1996) 15–22. doi: 10.1007/BF00726722.

[24] V. Gutmann, Solvent effects on the reactivities of organometallic compounds, Coord. Chem. Rev. 18 (1976) 225–255.

[25] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347. doi:org/10.1002/jcc.540141112.

[26] J.-D. Chai and M. Head-Gordon. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, Chem. Phys. 10 (2008) 6615-6620. doi:10.1039/B810189B.

[27] A.D. McLean and G.S. Chandler. Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11-18. J. Chem. Phys. 72 (1980) 5639-48. doi:10.1063/1.438980.

[28] K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople. Self-Consistent Molecular Orbital Methods. 20. Basis set for correlated wave-functions. J. Chem. Phys. 72 (1980) 650-54. doi:10.1063/1.438955.

[29] T. Yanai, D. Tew, and N. Handy. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). Chem. Phys. Lett. 393 (2004) 51-57. doi: 10.1016/j.cplett.2004.06.011.

[30] G. Scalmani and M.J. Frisch. Continuous surface charge polarizable continuum models of solvation. I. General formalism, J. Chem. Phys. 132 (2010) 110–114. doi:10.1063/1.3359469.

[31] http://www.chemcraftprog.com.

[32] N.A. Bumagina, E.V. Antina, M.B. Berezin, A.A. Kalyagin. Influence of structural and solvation factors on the spectral-fluorescent properties of alkyl-substituted BODIPYs in solutions, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 173 (2017) 228–234. DOI: 10.1016/j.saa.2016.09.026.

[33] B. Guo, X. Peng, A. Cui, Y. Wu, M. Tian, L. Zhang, X. Chen, Y. Gao. Synthesis and spectral properties of new boron dipyrromethene dyes, Dyes and Pigments. 73 (2007) 206-210. org/10.1016/j.dyepig.2005.11.007.

[34] Y. Chen, L. Wan, D. Zhang, Y. Bian, J. Jiang. Modulation of the spectroscopic property of Bodipy derivates through tuning the molecular configuration, Photochem. and Photobiol. Scien. 10 (2011) 1030–1038. doi:10.1039/C1PP00001B.

[35] A. Loudet, K. Burgess, BODIPY dyes and their derivatives: syntheses and spectroscopic properties., Chem. Rev. 107 (2007) 4891–932. doi:10.1021/cr078381n.

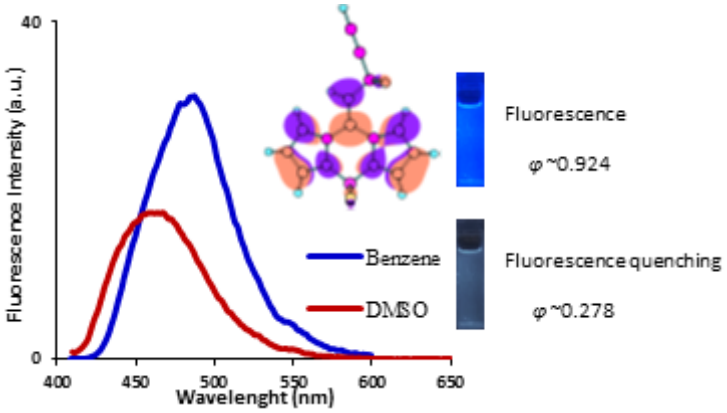
[36] E.V. Antina, M.B. Berezin, N.A. Dudina, S.L. Burkova, and A.Yu. Nikonova. Synthesis, Spectral-Luminescent Properties of B(III) and Zn(II) Complexes with Alkyl- and Aryl- Substituted Dipyrrins and Azadipyrrins, Rus. J. of Inorg. Chem. 59 (2014) 1187–1194. doi: 10.1134/S0036023614100027.

[37] C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, fourth ed., Wiley-VCH Verlag GmbH & Co. KGaA, 2011.

[38] B. Guo, X. Peng, A. Cui, Y. Wu, M. Tian, L. Zhang, X. Chen, Y. Gao, Synthesis and spectral properties of new boron dipyrromethene dyes, Dye. Pigment. 73 (2007) 206–210. doi:10.1016/J.DYEPIG.2005.11.007.

[39] J. Rumble CRC handbook of chemistry and physics, 99th Edition. – CRC press. (2018) 1550 p.

Graphical abstract



[40]

Highlights

- *Meso*-propargylamino-BODIPY **1** demonstrates the high sensitivity to the nature of the media.
- The dye fluorescence quenching increases with increasing the solvent proton and electron donor ability.
- Supramolecular complexation leads to the BODIPY **1** fluorescence quenching in polar medium.
- BODIPY **1** is recommended as a new fluorescent sensor of specific electron and proton donor molecules.